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SECOND QUARTERLY LETTER REPORT

THERMODYNAMIC PROPERTIES OF PROPELLANT COMBUSTION PRODUCTS

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INTRODUCTION

The objective of this program is to provide thermodynamic data for species which are potentially important combustion products of advanced chemical propulsion systems. Heat of formation and entropy data for species of interest are obtained from equilibrium studies carried out by effusion and free evaporation methods and by high-temperature mass spectrometry.

TECHNICAL PROGRESS

I. Gaseous Dihalides

The thermodynamic properties of many of the gaseous alkaline earth dihalides cannot be accurately calculated at present because of major uncertainties in the geometrical structures and bending frequencies. We are attempting to obtain accurate entropies of vaporization and sublimation that can be used in conjunction with condensed phase entropies to test the structural and vibrational assignments of the dihalides.

The vapor pressures of crystalline MgF_2, CaF_2 and SrF_2 are being measured by the torsion-effusion method in order to obtain accurate data over as wide a range as possible. High-purity optical-grade samples are being used. Available literature data for these substances are somewhat discordant, and some data do not cover a large enough temperature range (below the melting point) for accurate second-law analysis. By limiting the analysis to the sublimation pressures, one eliminates errors in the thermal properties of the liquid phases, as well as possible errors in vapor composition at the higher pressures. The vapor pressure measurements are nearly completed, and a preliminary analysis yields experimental vapor entropies for MgF_2 and CaF_2 which are consistent with linear structures and with doubly degenerate bending frequencies of about 175 and 120 cm^{-1}, respectively. These results are in agreement with recent spectroscopic work[1] which showed the bending frequencies to lie below 200 cm^{-1} and which showed only one infrared-active stretching frequency for each molecule. The absolute entropy of $SrF_2(g)$ could not be evaluated from the vaporization data because the entropy of condensed SrF_2 is not presently available. However, the measured effusion vapor pressure of SrF_2 is virtually identical with that of CaF_2, as is

the liquid vapor pressure in the millimeter range,[2] so that the entropies of vaporization of SrF_2 and CaF_2 must be very nearly equal. This would lead one to conclude that SrF_2 is also linear, although the evidence is not as clear in this case. Matrix infrared spectra[1] offer more definitive evidence for linear $SrF_2(g)$. It would appear on the surface that the vaporization data and infrared spectra are in conflict with the results of electric deflection experiments[3] which indicated CaF_2 and SrF_2 to be polar and, hence, nonlinear molecules. However, experimental uncertainties in the vaporization data would allow an X-M-X bond angle as small as 170°, and this might satisfy the polarity requirement of the deflection experiments.[3] A more detailed summary of the implications of the vapor entropy data will be given when the measurements on the difluorides are completed. The measurements will be extended to include BaF_2.

High-purity samples of anhydrous $BaCl_2$ and $SrCl_2$ are being prepared in sufficient quantity for low-temperature calorimetric measurements to be made in the laboratory of Prof. E. F. Westrum at the University of Michigan. Third-law entropies derived from the calorimetric data will be used in conjunction with vapor pressure data obtained earlier to evaluate the absolute entropies of the gaseous dichlorides. This will permit a more direct check of the structural and vibrational frequency assignments of these molecules.

II. BF_3 Mass Spectrum

The mass spectrum of BF_3 is given in Table I for a number of temperatures from room temperature to 1981°K. Considerable uncertainty exists in the relative intensities given, due to the difficulty of measuring shutter-dependent intensities in the presence of the much larger contributions from steady-state BF_3 background. However, the data are sufficiently accurate to indicate that at the higher temperatures the BF^+ relative intensity is an order of magnitude larger than it is at room temperature. The change could be due either to the effect of temperature on the mass spectrum of BF_3, or to the production of BF(g) by thermal decomposition of the trifluoride. The relative importance of these two effects and equilibria among the lower fluorides will be studied in more detail by the beam-modulation technique described below.

TABLE I

TEMPERATURE DEPENDENCE OF THE MASS SPECTRUM OF BF_3

m/e	Ion			Relative Intensity (Ionizing Voltage = 70V)				
		$296^\circ K^a$	$296^\circ K$	$819^\circ K$	$1417^\circ K$	$1756^\circ K$	$1934^\circ K$	$1981^\circ K$
68	BF_3^+	5.4	12.4	4.2	5.5	3.5	3.6	5.2
49	BF_2^+	100.0	100.0	100.0	100.0	100.0	100.0	100.0
30	BF^+	2.2	1.2	<2	30.0	14.0	30.0	42.0
11	B^+	2.0	2.8	3.1	3.8	4.1	7.5	7.2

[a] For total intensities. Remaining spectra are for shutter-dependent intensities.

III. Beam dulation Technique

A major share of the effort this quarter has been devoted to modification of the mass spectrometer for beam-chopping,[4] as mentioned previously. By means of this technique, the neutral effusion beam is modulated by the action of a chopper wheel so that ion signals produced from the beam gases have a specific frequency and phase. This allows one to use ac circuitry to discriminate between beam and background signals, since the latter are dc. In addition, it should be possible to obtain more information about neutral precursors of ions from phase angle shifts introduced by time-of-flight effects. It is believed that beam modulation will greatly increase the effectiveness of the mass spectrometer for high-temperature studies.

The chopper will be interposed between Knudsen and ion source compartments. A chamber for housing the chopper has been designed and is presently being constructed. The ac circuitry has been ordered and will be delivered within the next quarter. The chopper compartment will be provided with a separate differential pumping system, and, in addition, the Knudsen compartment will be modified to accept a new high-speed diffusion pump and high-conductance cold trap. It is expected that the new system will be put into operation within the next quarter.

IV. Major Accomplishments

Further information on the molecular constants of some gaseous difluorides was obtained and substantial progress was made on the beam-chopping modification to the mass spectrometer.

V. Problems Encountered

No major technical problems were encountered.

VI. Future Plans

Vaporization studies on the alkaline earth difluorides will be completed and measurements on aluminum carbide will be initiated. Work on the beam-modulation system will continue; mass spectrometric studies on aluminum and boron subhalides will be initiated when the modifications are completed.

VIII. Action Required by Government

None

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